

Deposition and Thermal Stability of DLC/Si-N Composite Films Synthesized Using a Sputtering-PBII Hybrid System

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Abstract

Diamond-like carbon (DLC) is a metastable amorphous material that exhibits unique properties. However, there are many limitations regarding the use of this material due to factors such as its tribological characteristics at high temperature and limited thermal stability. In this study, the thermal stability and tribological properties of DLC/silicon-nitrogen (DLC/Si-N) composite films were investigated and compared to those of pure DLC films. All the films were synthesized using a combination of radio frequency (RF) magnetron sputtering and plasma-based ion implantation (PBII) (a so-called sputtering-PBII hybrid system) which is newly developed by us. A high purity silicon nitride (99.9%) disk was used as the target, applying an RF power in the range of 500 - 700 W and a negative pulsed bias voltage of 5 kV to the substrate. An Ar-CH₄ mixture was used as the reactive gas. The CH₄ partial pressure was varied between 0 and 0.15 Pa, while the total gas pressure and total gas flow were fixed at 0.30 Pa and 30 sccm, respectively. The structures of the resulting films were characterized using Raman spectroscopy, while the thermal stabilities were assessed using thermogravimetric-differential thermal analysis (TG-DTA) and friction coefficients were obtained via ball-on-disk friction tests. The results indicate that the DLC/Si-N composite films produced in this work exhibit improved thermal stability relative to that of pure DLC owing to the presence of thermally stable atomic-scale Si-N compound in the carbon main flame networks. A DLC/Si-N film containing approximately 11 at.%Si and 18.5 at.%N shows good thermal stability in air over 800°C up to 1100°C, together with excellent tribological performance at 500°C in air. Overall, the data demonstrate that DLC/Si-N composite films offer improved thermal stability and superior tribological performance at high temperatures.

Keywords

Diamond-Like Carbon, DLC/Si-N, Tribology, Sputtering-PBII Hybrid System

1. Introduction

There have been many attempts to develop hard, heat-resistant, low friction thin films that can be used at high temperatures and under high loads. Among the potential candidates, diamond-like carbon (DLC) films exhibit excellent tribological properties, such as a high degree of hardness, low friction, good wear resistance, and low aggressiveness [1] [2]. Other helpful characteristics of these films include chemical stability and tunable electric resistance [3] [4] [5] [6] [7]. As a result, these materials have applications including cutting tools and metal molds. However, depending on the usage environment, there are still challenges such as adhesion to the substrate and limited friction durability, especially at temperatures above 300°C [8] [9] [10] [11], and DLC-composite films have been developed as a means of addressing these issues. The incorporation of silicon into DLC has overcome some of the stated drawbacks, including significantly reduced residual stress, while retaining the hardness, improving the thermal stability and delivering a low friction coefficient that is highly insensitive to changes in humidity [12] [13] [14]. When both silicon and oxygen are incorporated into DLC films, significant structural modifications occur. Other authors claim to have obtained a material that consists of an atomic-scale composite of random networks of carbon and silicon in which the carbon network is stabilized by hydrogen, while the silicon network is stabilized by oxygen. This type of structure is referred to as a diamond-like nanocomposite (DLN) [15] [16] [17]. The co-incorporation of silicon/oxygen into DLC films presents interesting mechanical, tribological and optical properties, as well as higher values of thermal stability and fracture toughness [18]. Further, Chen *et al.* reported that nitrogen-incorporated DLC films were extremely wear resistant with a low coefficient of friction [19]. The reduction in residual stress and the enhancement in thermal stability of nitrogen-incorporated DLC films were previously reported [20] [21] [22]. In our previous study [23], it was found that the silicon/nitrogen co-incorporated DLC films fabricated by PBII using acetylene (C_2H_2), tetramethylsilane (TMS, $Si(CH_3)_4$) and nitrogen (N_2) as plasma sources showed the good thermal stability under a temperature environment of about 600°C that has never been reported before. However, it is of interest to develop DLC films that can achieve thermal stability in the region exceeding this temperature.

In the present study, a DLC film was combined with the thermally stable Si-N system [24] [25] to improve more the heat resistance of the original film. A sputtering-plasma based ion implantation (PBII) hybrid process developed in our laboratory [26] was employed in conjunction with Si_3N_4 to prepare DLC/Si-N composite films, and the heat resistance and other properties of these films were assessed.

2. Experimental

Figure 1 shows a schematic diagram of the equipment used in this work. The experimental device contained a substrate holder for use during the PBII process attached at the top and connected to DC pulse and radio frequency (RF) power supplies. The conditions for the fabrication of the film are presented in **Table 1**. To ensure adhesion of the film to the substrate, the film was subjected to an Ar ion bombardment for 10 min as a pretreatment. Following this, CH₄ was introduced at approximately 1 Pa, a pulsed -20 KV DC bias was applied and PBII was carried out for 1 h.

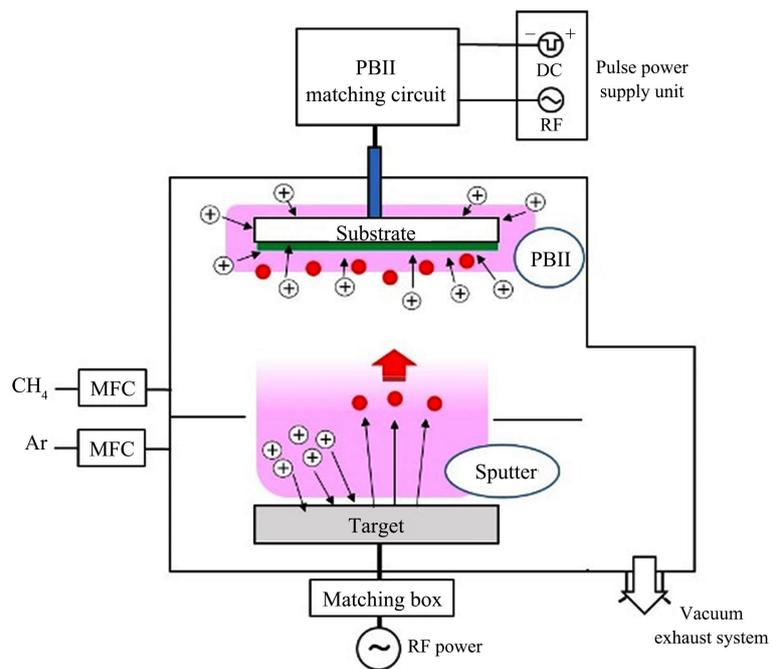


Figure 1. Schematic illustration of Sputtering-PBII Hybrid System used in this experiment.

Table 1. Deposition conditions.

[Sputtering]	
Target	Si ₃ N ₄
RF Power	500/700 W
Target-Substrate Distance	85 mm
[PBII]	
Pulse Frequency	1.0 kHz
DC Pulse Bias	-5.0 kV (Width: 5 μ s, Delay: 25 μ s)
Pulse RF Power	300 W (Width: 50 μ s, Delay: 25 ns)
Ar Gas Flow Rate	30 sccm
CH ₄ Gas Flow Rate	10, 15, 20 sccm
Deposition Time	120 min

The compositions of the resulting films were quantitatively assessed using energy dispersive X-ray spectroscopy (EDS: JSM-IT 300), with a 600 s analysis at a 15.0 kV acceleration voltage and 10 mm working distance. The heat resistance of each film was determined using thermogravimetric analysis-differential thermal analysis (TG-DTA). Each film was first formed on aluminum foil and then isolated by dissolving the foil in an aqueous hydrochloric acid solution. During the TG-DTA trials, the specimen was heated to 800°C (or as high as 1100°C in some cases) in air. The residue deposited in the crucible after the thermal test was then analyzed by EDS using similar instrumental parameters to those described above.

Samples that exhibited minimal mass loss during the TG-DTA investigations were used for friction assessments, which were performed with a ball-on-disk type friction test apparatus. In preparation for these analyses, each film was formed on a superhard material (WC-Co) under the same conditions used to produce the original films, and heat-treated at 500°C for 30 min in an electric furnace prior to the friction test. The friction analysis was conducted using a load of 1 N, a rotation rate of 100 rpm, a total of 6000 rotations (or laps), a 3 mm radius of rotation under air and with an Al₂O₃ ball (ø6 mm). The vibration friction wear tester called SRV (Schwingungs Reihungund und Verschleiss) tester, which is used as a tester for evaluating tribocoating in fields such as the automobile industry. The samples used for the evaluation were those in which a film was formed on superhard material (WC-Co) substrate (12 × 12 × 5) with a polished surface under the three types of film-forming conditions that were found to have excellent heat resistance in the previous report. The friction test conditions Load 10 N, vibration width 50 μm, frequency 50 Hz, test time 600 seconds. The sample temperature was set to 200°C in consideration of the application field. The structure of the films was analyzed using Raman spectroscopy (JASCO NRS-1000 DT) at an excitation wavelength of 532 nm and a spot size of 4 μm. The Raman spectra in the wave number region were deconvoluted from 1000 - 1800 cm⁻¹ into the Gaussian D and G peaks. The integral area under the D and G peaks was determined by curve fitting.

3. Results and Discussion

The films employed in this work were generated using graphite as the target material. The TG data showing mass changes as functions of temperature for both the DLC/Si-N composite and pure DLC films are shown in **Figure 2**. Sample 1 (700 W, 10 sccm) underwent a large mass loss between 300°C and 550°C and was completely oxidized at 800°C, with no residue left after the test. In contrast, samples 2 (700 W, 15 sccm), 3 (500 W, 10 sccm) and 4 were found to be stable up to 800°C, such that only a small mass loss was observed. However, when these same specimens were heated to 1100°C, samples 3 and 4 demonstrated a significant mass loss, while sample 2 underwent only a small mass loss. The DTA data showed that each of samples 3 and 4 also produced a broad exothermic peak between 700°C and 900°C (data not shown), which can be attri-

buted to the combustion of the films. Sample 2 did not generate an exothermic peak above 600°C, indicating excellent heat resistance.

Prior to the TG-DTA analyses, sample 2 (which demonstrated superior heat resistance), was heated at 800°C and 1100°C, and the changes in the composition of the film residue left in the crucible at both temperatures are graphed in **Figure 3**. Following heating at 1100°C, the residue had a lower C concentration compared to that before the test. However, the reduction in C content was only approximately 50% despite the high temperature that was applied. The O content was found to be as low as 11.3%, confirming relatively minimal oxidation. The residues recovered after heating at 800°C and 1100°C also showed very similar compositions, demonstrating that sample 2 had good heat resistance.

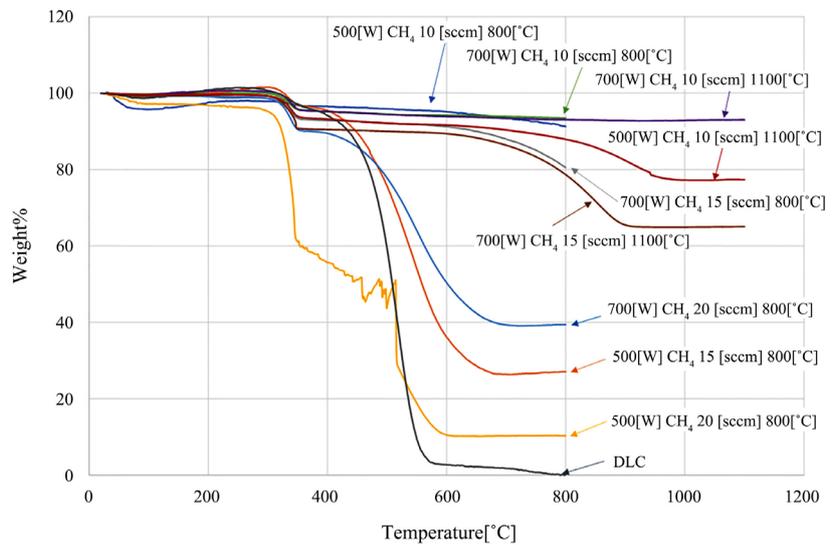


Figure 2. Changes in thermogravimetric curves of the films.

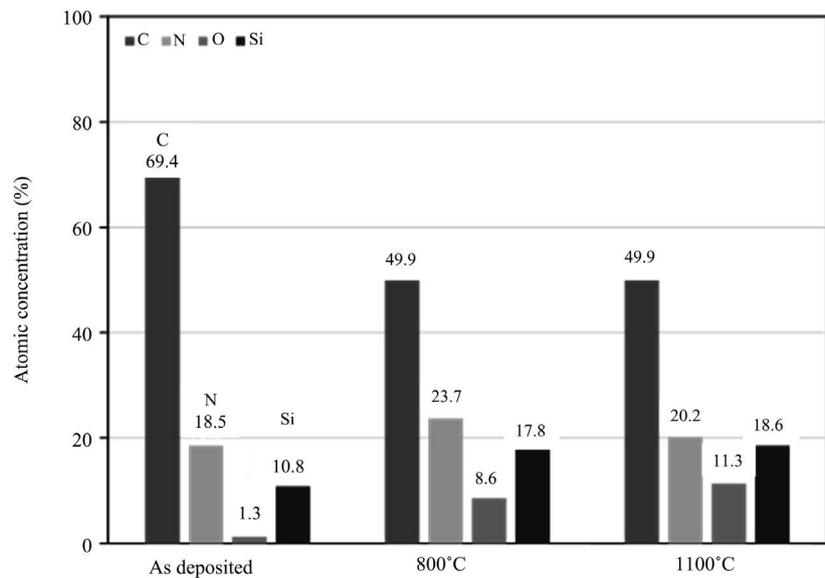


Figure 3. EDS analytical results of as deposited, after 800°C heating and after 1100°C heating in 700 [W] CH₄ 10 [sccm].

Figure 4 shows the ball-on-disk friction test results for samples 2, 3 and 4, and demonstrates that all three films had relatively low friction coefficients in the range of 0.1 - 0.3. However, the friction coefficient for sample 3 was the lowest.

Figure 5 shows the friction test results obtained from films after heating at 500°C. Here, sample 4 is seen to have had a much higher friction coefficient after heating compared to the value immediately following fabrication. In contrast, the friction coefficients of samples 2 and 3 were more stable, and actually decreased from their original values. The friction coefficient for sample 3 increased to approximately 0.6 during the initial stage of the test, and this effect is attributed to the change in the composition of the material close to the film surface, due to oxidation from heating. This oxidation resulted in a film structure that was easily worn off when heat was applied. As this layer was worn away, the underlying layers that were not affected by heating became the test surface, leading to less friction.

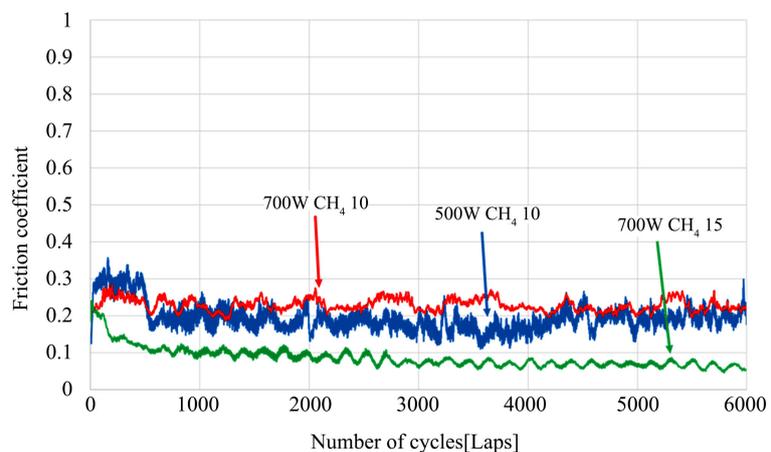


Figure 4. Changes in friction coefficients of three kinds of films at room temperature.

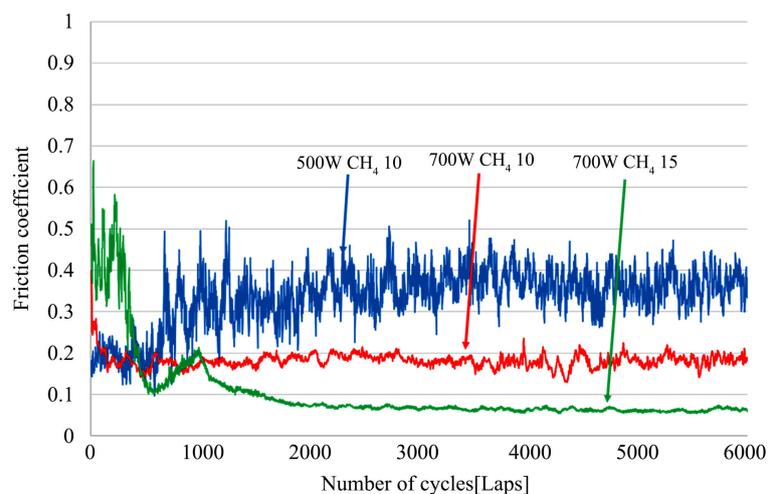


Figure 5. Changes in friction coefficients of three kinds of films after heating of 500°C.

Figure 6 shows the change of the friction coefficient with respect to the number of friction of each sample. Although the friction test was repeated three times, the reproducibility was good. Sample 3 had good heat resistance, but the friction coefficient was high and wear was also observed in the ball-on-disk friction test conducted separately, but this was also the case in this SRV test. The film surface was damaged during the test. In comparison, both the samples 1 and 2 showed stable friction behavior in this evaluation, and although there was a difference in the coefficient of friction, no damage was found on the film surface side.

It was confirmed that it was excellent in wear resistance. The friction coefficient of sample 1 is about 0.2 - 0.25, which is higher than that of sample 2, but this tendency was the same in the ball-on-disk test.

Figure 7 shows the Raman spectroscopic results of samples 1. In the fig, spectra at room temperature, 800°C and 1100°C are also shown for comparison. From this result, a broad peak composed of D-Band and G-Band, which is common in all DLC films, is confirmed in all films. The as-deposited film shows the Raman spectrum found in typical DLC films. On the other hand, after heating at 800°C the peak is broad. In previous studies, there were no reports that two bands of D and G were observed even when the DLC film heated at 800°C. After heating at 1100°C, it was found that D and G-band peak show splitting and G-band peak position shifting to the lower wavenumber side compared to DLC. The changes in these spectra might correlate with graphitization of amorphous carbon (graphite-like spectral shape). As described above, it was confirmed that the carbon network of the DLC film exists without breaking even at a high temperature of 1100°C.

4. Conclusion

DLC/Si-N composite films were formed by adding the thermally stable compounds Si and N to DLC films, so as to enhance the heat resistance of the films.

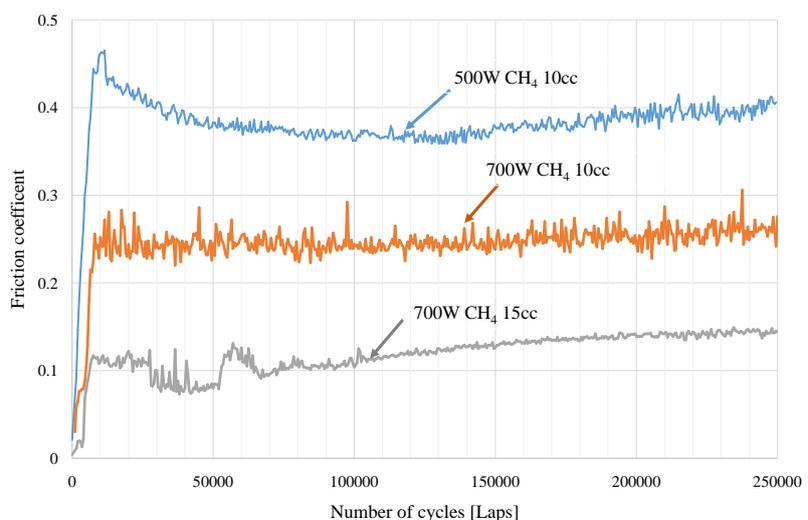


Figure 6. Vibration friction and wear tester SRV evaluation.

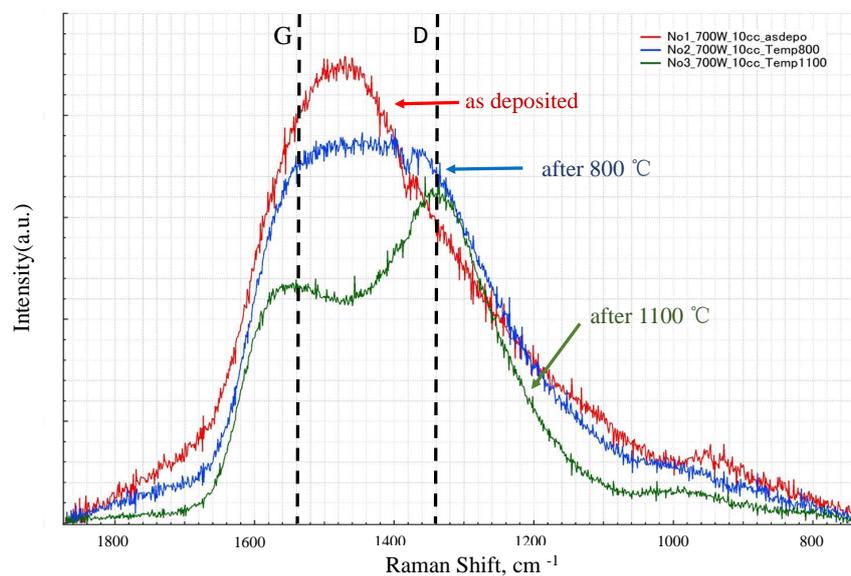


Figure 7. Results of Raman spectroscopy as deposited, after 800°C heating and after 1100°C heating in 700 [W] CH₄ 10 [sccm].

TG-DTA data showed that the heat resistance of the DLC/Si-N composite films was superior to that of a pure DLC film. In particular, the film formed at an RF sputtering power of 700 W and a CH₄ flow rate of 10 sccm exhibited excellent heat resistance together with a minimal mass loss at temperatures as high as 1100°C. This same film retained as much as 49.9% C with an O content as low as 11.3%, even after heating at 1100°C. There was no significant change in these values compared to the composition obtained after heating at 800°C. Ball-on-disk frictional wear tests showed that the coefficient of friction of an optimized film was unchanged by heating to 500°C and Tribological properties of DLC/Si-N films with good heat resistance were evaluated using an SRV vibration friction wear tester in consideration of practical application. As a result, it was confirmed that the film with excellent heat resistance also has good wear resistance, because the results indicate that the DLC/Si-N composite films produced in this work exhibit improved thermal stability relative to that of pure DLC owing to the presence of thermally stable atomic-scale Si-N compound in the carbon main flame networks.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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